

Direct evidence of relaxation anisotropy resolved by high pressure in a rigid and planar glass former

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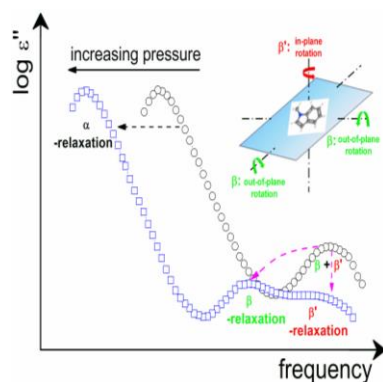
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ABSTRACT: Rigid molecular glass-formers with no internal degrees of freedom nonetheless have a single secondary β -relaxation. For a rigid and planar molecule, 1-methylindole (1MID), although a secondary relaxation is resolved at ambient pressure, its properties do not reproduce the rules established for rigid molecules reported in early studies. By applying pressure to the dielectric spectra of 1MID, we find the single secondary relaxation splits into two. The slower one is pressure sensitive showing connections to the α -relaxation as observed in other rigid molecules, while the faster one is almost pressure insensitive and becomes dominant at ambient pressure. **As the two secondary relaxations are identified to associate with the out-of-plane and in-plane rotations, the time-scales of different anisotropic motions in the glasses of rigid molecules are separated for the first time by increasing density.**

TOC GRAPHICS



KEY WORDS: Glass transition, Johari-Goldstein β -relaxation, rigid molecule, pressure

Secondary relaxations having properties strongly connected to structural α -relaxation are important for fundamental understanding of glass transition, and are classified as the Johari-Goldstein (JG) β -relaxation¹ to distinguish them from the trivial secondary relaxations originating from intramolecular degrees of freedom. Examples of the connections in the liquid state include invariance of the ratio of its relaxation time τ_β to the α -relaxation time τ_α to variations of pressure and temperature while keeping τ_α constant,² and both τ_β and τ_α are functions of the same product variable T/ρ^γ , where ρ is the density and γ is a material constant.^{3,4} In the glassy state, the JG β -relaxations are instrumental for cold crystallization, a serious concern of the pharmaceutical research community,² and a rate-limiting factor in producing ultrastable glasses by vapor deposition.⁵ Thus the JG β -relaxations have broad connections to active research areas and impacts as well. Prior to the study of the dynamics in rigid molecular glass-formers by JG,⁶ it was commonly believed that all secondary β -relaxations originate from some motion of a part of the molecule. The discovery of the presence of a prominent secondary relaxation in rigid molecules such as chlorobenzene by JG four decades ago reveals its origin from the motion of a whole molecule. The fundamental importance of the secondary relaxation also has been recognized from the strong connections to the thermal stability,⁷ the elastic and deformation behaviors⁸⁻¹⁰ in glasses, and to the structural α -relaxation.¹¹⁻¹³ Suggested by the Coupling Model (CM)¹ and established empirically, τ_β is found to be quantitatively related to $\tau_\alpha^{2,11-13}$ in the Kohlrausch correlation function, $\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_{KWW}}]$ of the α -relaxation, where β_{KWW} is a fractional exponent. So far all rigid molecules studied experimentally including chlorobenzene,⁶ 2-picoline,¹² quinaldine,¹³ benzonitrile,^{14,15} ortho-terphenyl,^{6,16} toluene,¹⁷ adamantanone,^{18,19} 1-fluoro-adamantane,²⁰ hexa-substituted benzenes,²¹ a rigid, asymmetric, diatomic toy molecule assessed by simulation,²² show a *single* secondary relaxation, which verifies the connections of the α and β - relaxations. The α and β - relaxation connections are also verified in some metallic glasses, such as $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ ²³ and $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ ²⁴, as well as in ionic liquid conductors²⁵, where a well separated β - relaxation is observed. In all these cases not only orientational

but also translational motions are involved. Similarly, the α and β -relaxation connections are verified as well in many non-rigid glass-formers.^{2,14,26-28} For the purpose of distinguishing the secondary relaxation having this property from others that have not, the former is called the JG β -relaxation,^{1,11,14} which is usually the slowest among secondary relaxations.

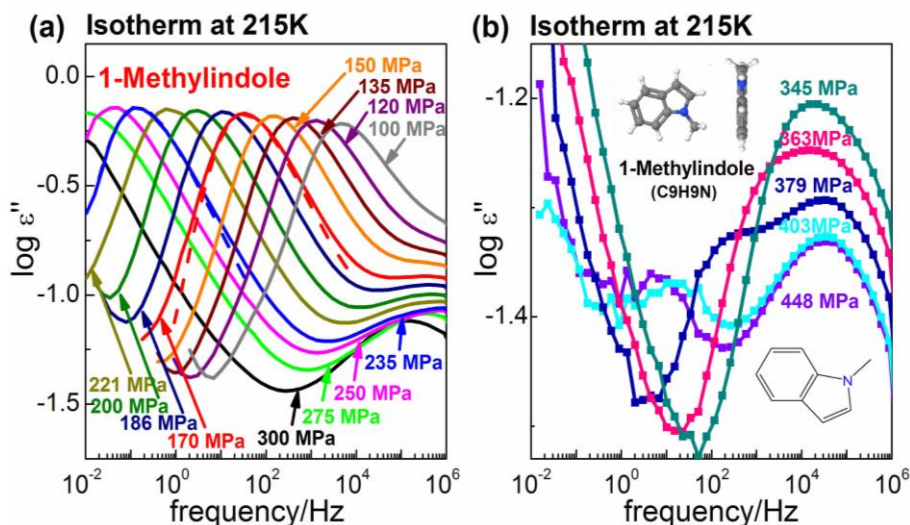


Figure 1. Isothermal dielectric spectra of 1MID at $T = 215$ K. (a) Isothermal spectra recorded for $100 \leq P \leq 300$ MPa (solid lines), and two sets of data measured at ambient pressure and $T = 185$ K (blue dashed line) and $T = 191$ K (red dashed line) reported in Ref.²⁹ are added. (b) Isothermal spectra recorded for $345 \leq P \leq 448$ MPa. The molecular structure of 1MID is shown in the inset.

Yet, in a recent study of the rigid and planar glass-former, 1-methylindole (1MID), with structure shown in the inset of Figure 1, a single secondary relaxation was resolved in the isothermal dielectric spectra, but its properties are at odds with those of the β -relaxations²⁹ of rigid molecules. For example, compared with toluene, which was viewed as the only glass-former with a planar structure without intramolecular degree of freedom,^{30,31} the separation of the β -loss peak relative to the α -loss peak of 1MID is more than one order of magnitude larger at T_g , albeit comparable relaxation dispersions were identified for the two molecules.³² More strikingly, when diluted by apolar molecules of larger and smaller sizes, the resolved β -relaxation time shows exactly the same temperature dependence as in the

pure 1MID.³³ Given the fundamental importance JG β -relaxations and broad connections, it is crucial to identify its nature in 1MID and clarify the origin of the resolved non-JG β -relaxation. Notwithstanding a conceivable explanation was proposed from our recent studies,^{29,33} a direct evidence is still not available to rationalize the remarkable anomaly. In this letter, we report experimental efforts to separate the supposedly slower JG β -relaxation from a faster β -relaxation of 1MID by elevating pressure and temperature. The slower secondary relaxation found indeed has properties identifiable with the JG β -relaxation observed in the rigid molecules reported in earlier studies,^{2,12-15} and the origin of the additional and faster secondary relaxation in the rigid 1MID not seen before in any other rigid molecular glass-formers is clarified.

The dynamic and thermodynamic properties of 1MID at ambient pressure have been reported in Refs.^{29,33} showing $\beta_{KWW} = 0.53$ near the glass transition temperature $T_g = 181$ K. Its chemical structure (Figure 1b) shows that it is a totally rigid and planar molecule, and the absence of intramolecular transition, tautomers, and conformers was demonstrated.^{34,35} We performed isothermal dielectric relaxation measurements at elevated pressures P . Representative loss spectra, $\varepsilon''(f)$, at 215 K are presented as an example in Figure 1. At lower pressures of up to 300 MPa where 1MID remains in the liquid state, a single secondary loss peak is present together with the α -loss peak as shown in Figure 1a. The dashed lines represent two sets of data at ambient pressure of 0.1 MPa,²⁹ chosen to have the same peak frequencies as the data at $P = 170$ MPa and $P = 235$ MPa. The invariance of the frequency dispersion of the α -relaxation to changes of P and T at constant α -relaxation time τ_α exhibited is a general property of van der Waals glass-formers.^{2,36} On further increase of P in Figure 1b, the secondary loss peak shows significant reduction of its intensity with attendant broadening on the low frequency side. At 379 MPa and beyond, a slower secondary relaxation is resolved and moves rapidly to lower frequencies with increasing pressure. In contrast, the peak frequency of the faster one seems to be pressure insensitive.

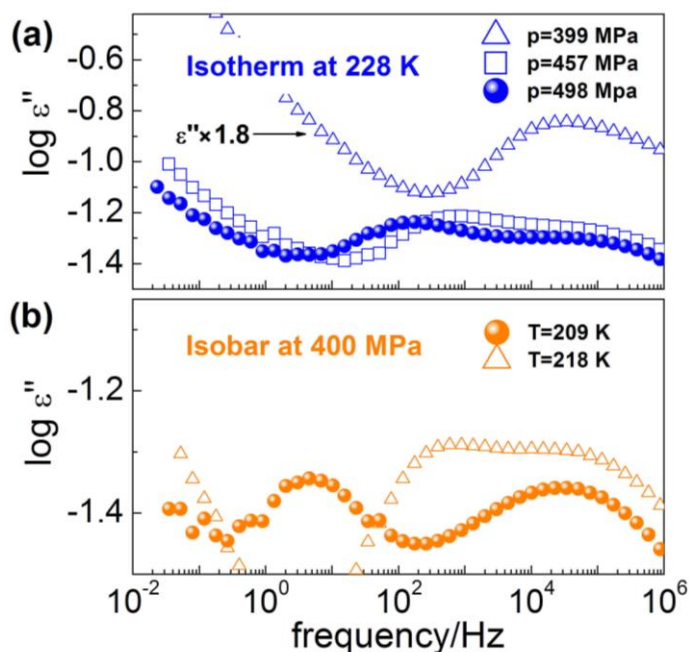


Figure 2. Isothermal and isobaric dielectric loss data of 1MID showing the separation of two secondary relaxations at high pressure and low temperature. (a) Isothermal measurements at $T = 228$ K. (b) Isobaric measurements at $P = 400$ MPa. In panel (a), the data at $P = 399$ MPa are shifted vertically by a factor of 1.8.

We present the isothermal data at $T = 221$ K (Figure S1 in Supporting Information) and at $T = 228$ K (Figure 2a) as a function of frequency at three pressures, and isobaric data at 400 MPa as a function of frequency at two temperatures (Figure 2b). By the two different ways to get into the glassy state, the slower secondary relaxation is resolved at sufficiently high pressure. To distinguish the two secondary relaxations of the rigid molecule we name the faster one β' -relaxation. Now we learn from the changes in the isothermal data shown in Figure 1, Figure 2a, and also Figure S1, that τ_β is too close to $\tau_{\beta'}$ at lower pressures, and the same applies to the isobaric data at 400 MPa at the higher temperature (Figure 2b). Consequently the β -relaxation is eclipsed by the β' -relaxation at lower pressures and *a fortiori* at ambient pressure, as found previously.²⁹ The much weaker T -dependence of $\tau_{\beta'}$ than τ_β at 400 MPa can be inferred from Figure 2a-b. The remarkable pressure insensitivity of $\tau_{\beta'}$ is a clear indication that it is a local motion weakly coupled to density.

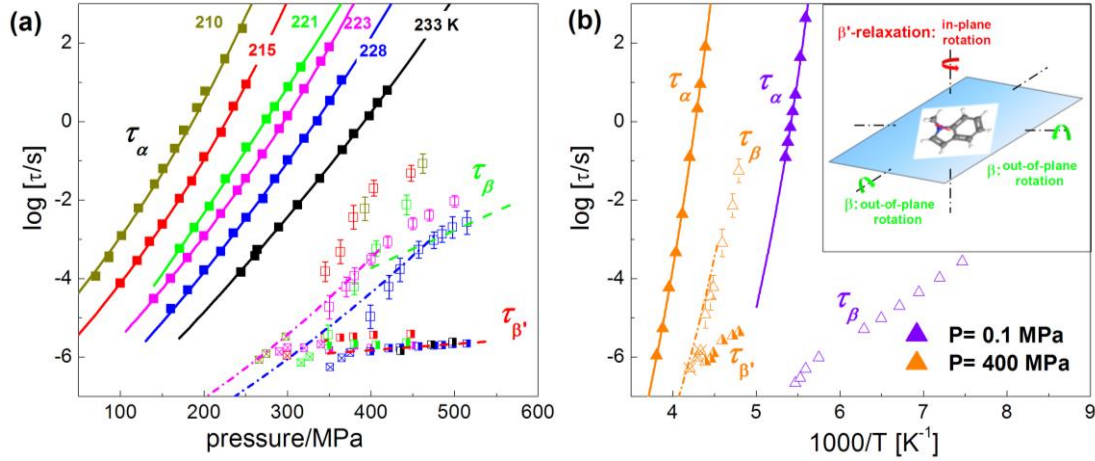


Figure 3. Pressure (a) and temperature (b) dependences of α , β - and β' -relaxations for 1MID obtained at six different temperatures ($T = 210$ K, 215 K, 221 K, 223 K, 228 K, and 233 K) and at two different pressures ($P = 0.1$ MPa, and 400 MPa). Full, empty and empty-full symbols refer to the α , β - and β' -relaxations, respectively. The empty symbols adorned by the \times sign represent the relaxation times of the merging β - and β' -relaxations. In panel (a), only the β' -relaxation (the black empty-full squares) is seen at $T = 233$ K. In the inset of panel (b), two rotation modes for the planar 1MID are shown, and the direction of the dipole moment is shown as the in-plane red arrow. Solid lines are fits of T - and P -dependence of τ_α by the VFT equation (b) and its analogue (a). The green and red dashed lines in panel (a) are linear fits of the pressure dependence of τ_β and $\tau_{\beta'}$ at $T = 228$ K. In both panels, the coupling model prediction for τ_0 has been calculated and reported as dashed-dotted lines with $n = 0.47$ applied.

The collection of isothermal spectra obtained over a wide range of pressures at each of the six temperatures $T = 210, 215, 221, 223, 228$, and 233 K was analyzed by fitting the α -relaxation with the Fourier transform of the KWW function and the Havriliak-Negami (HN) function while fitting the β - and β' -relaxations with the sum of two HN functions.^{37,38} The isothermal relaxation times, $\tau_\alpha(P, T)$, $\tau_\beta(P, T)$, and $\tau_{\beta'}(P, T)$, deduced from the fits are presented as functions of P in Figure 3a. The same color of the symbols for data obtained at the same temperature T is adopted to distinguish the different sets. Whenever the β -relaxation is resolved from the β' -relaxation, the full and empty symbols denote τ_β and

$\tau_{\beta'}$, respectively. The solid lines are the fits by an analogue of the Vogel-Fulcher-Tammann (VFT) equation to the P -dependence of τ_{α} .^{2,39,40} Defining the glass transition pressure P_g (temperature T_g) as the pressure (or temperature) at which $\tau_{\alpha} = 100$ s,⁴¹ we obtain the P_g values for each isothermal condition and the T_g values for each isobaric condition. All the results are used to describe the pressure dependence of T_g (Figure S2 in Supporting Information). Figure 3a shows the significant P -dependence of τ_{β} and the lack of it in the case of $\tau_{\beta'}$, collectively for all isothermal data. At $T = 215, 221, 223$ and 228 K, we managed to acquire data at high enough pressures to show the crossing of $\tau_{\beta}(P,T)$ from a stronger to a weaker P -dependence, which corresponds to vitrification of 1MID by pressure at P_g . In contrast, $\tau_{\beta'}(P,T)$ is unchanged upon crossing P_g , reaffirming its insensitivity to density change. In the case of the isothermal data at $T = 233$ K, the pressure could not be raised higher than 500 MPa to resolve the β -relaxation.

The disparity in the P -dependence between τ_{β} and $\tau_{\beta'}$ naturally leads to the merging of the β -relaxation with β' -relaxation upon decreasing pressure. The tendency to merge is seen in Figure 1 and Figure 2a-b by the change to a single broad peak at some lower pressures in the isothermal data at $T = 215$ and 228 K. The relaxation times $\tau_{\beta\beta'}$ of these merged $\beta\beta'$ peaks are represented by the same symbols and colors but adorned by the \times sign to distinguish $\tau_{\beta\beta'}$ from τ_{β} (closed symbols) and $\tau_{\beta'}$ (open symbols) obtained from the fitting by two HN functions in Figure 3a. The milder P -dependence of $\tau_{\beta\beta'}$ compared with τ_{β} is a consequence of the tendency of the β -relaxation to merge with the β' -relaxation.

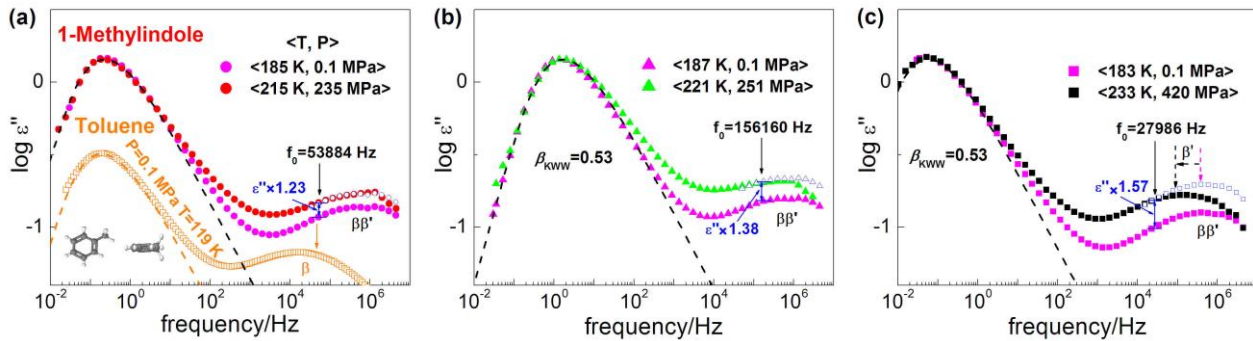


Figure 4. Dielectric loss spectra of 1MID measured at various temperature and pressure combinations under the condition of the same α -loss peak frequency f_α . In panel (a), the data of toluene are shown together with its structure. The black dashed lines in each panel represent the KWW fits using the same exponent β_{KWW} of 0.53. The black solid vertical arrows in each panel indicate the calculated JG β -relaxation frequency f_0 for 1MID calculated by the CM. The orange arrow in panel (a) marks the calculated f_0 for toluene. The blue open symbols (circles in panel (a), triangles in panel (b) and squares in panel (c)) are the total ambient-pressure $\beta\beta'$ -relaxation peaks shifted vertically. The magenta and black dashed vertical arrows in panel (c) mark the shift of ambient-pressure $\beta\beta'$ -loss peaks and the high pressure ones.

The conundrum encountered in the study of the rigid and planar 1MID at ambient pressure is the faster β' -relaxation, not present in any of the rigid molecular glass-formers studied before. Earlier studies of toluene exhibit anisotropic motion in the liquid state.^{30,31} For example, using nuclear magnetic resonance spin-lattice relaxation experiments, Hinze *et. al.* found the β -relaxations in toluene show a pronounced anisotropy at temperatures below T_g or at very high temperatures above $1.2T_g$.^{31,42} Our results in Figure 4 show that the anisotropy in the β -relaxation of 1MID becomes more obvious at lower temperature (or higher pressure), where the energy barrier to overcome for relaxation is higher due to densification of the sample.

The properties of the β' -relaxation in 1MID, together with the absence of intramolecular transition, tautomers and conformers demonstrated before by experiments,^{34,35} leave the in-plane rotation (see the inset of Figure 3b) as the only possible origin of the β' -relaxation in this planar molecule of rather large size.²⁹ The possibly large angular displacements of the in-plane rotation gives rise to the more intense β' -relaxation to eclipse the JG β -relaxation nearby, which involves out-of-plane rotation of 1MID. The in-plane and out-of-plane rotations are schematically depicted in Figure 3b. The origin of the β' -relaxation from in-plane rotation of a planar rigid 1MID molecule is supported by the small activation

volume of $9.7 \pm 2 \text{ \AA}^3/\text{molecule}$ estimated from the weak pressure dependence of $\tau_{\beta'}$ in Figure 3a,⁴³ which is about one eighth of the activation volume for the JG β -relaxation. We could expect that the activation energy for rotation could be quite different for the two kinds of motions, especially at high density. In-plane rotations also have been found in the nematic phases of liquid crystals such as 4-cyano-4-n-pentylbiphenyl (5CB) and discotic liquid crystals probed by dielectric study.⁴⁴⁻⁴⁷

Figure 4 shows the comparison of the relaxation spectra determined at elevated pressures and at ambient pressure under the condition of the same α -loss peak frequency f_α . All α -loss peaks are observed to superpose well to show invariance of the frequency dispersion to pressure. The total $\beta\beta'$ -loss peaks measured under ambient pressure are shifted vertically by a constant to match the high-pressure data, and this is shown in Figure 4a-c. In Figure 4a, the shifted ambient-pressure $\beta\beta'$ -loss peak and the 235 MPa one overlap almost entirely. At higher pressures of 251 and 420 MPa in Figure 4b and 4c, the right flank of the shifted ambient-pressure $\beta\beta'$ -loss peak become increasingly higher than that of the high-pressure one. Hence, by raising temperature and pressure, the intensity of the slower β -relaxation is effectively enhanced, in particular in the case of $T = 233 \text{ K}$ and $P = 420 \text{ MPa}$ (Figure 4c). In contrast, the strengths of the faster β' -relaxations do not vary much.

At constant f_α or τ_α , the total $\beta\beta'$ -loss peak become narrower as the temperature and pressure are increased in Figures 4b-c and Figure S3 (See Supporting Information). The narrowing of the $\beta\beta'$ -loss peak is caused by the shift of its right flank to lower frequency at higher pressure, while its left flank is practically unchanged. Since the left flank is effectively contributed by the slow β -relaxation, from its invariance to applied pressure we can infer that τ_β is invariant, hence invariance of the ratio τ_α/τ_β . On the other hand, the change of the right flank contributed by the faster β' -relaxation indicates it does not have such a relation to the α -relaxation. Established before as a general property of the JG β -relaxation,² the relation found for the slow β -relaxation in 1MID is another support of identifying it as the JG β -relaxation. Figure 4a also shows the data of toluene at ambient pressure because toluene has the same

β_{KWW} of 0.53 of the α -relaxation as 1MID³². The location of the slower β -relaxation $f_\beta \equiv 1/(2\pi\tau_\beta)$ of toluene is found to agree with the primitive frequency f_0 of the Coupling Model determined by $f_0 = (1/2\pi\tau_0) = (1/2\pi t_c^n \tau_\alpha^{1-n})$,^{2,15} where t_c is approximately 2 ps and $n = 1 - \beta_{KWW}$. The f_0 values for the 1MID spectra are also marked in the three panels. It is seen that the frequency of the pressure-sensitive slow β -relaxation is near the primitive frequency, whenever it is resolved from the total $\beta\beta'$ -loss peaks. In Figure 3, CM predictions for τ_0 , calculated for high pressure dataset using $n=0.47$ and fit curve for τ_α up to 10 ks, are reported matching quite well experimental values of τ_β .

It could be noted that in Figure 2 and Figure 4 an excess contribution with respect of the KWW fits between the high frequency flank of the α -loss peak and the manifestation of the $\beta\beta'$ -relaxation. Such a feature increases on increasing pressure paralleling what happens for the intensity of the β process. If that can be attributed to an additional process related to a different rotational mode or related to some cross-correlation terms of α - and β - processes, whose representation in terms of linear superposition is never adequate, is beyond the scope of the present paper but could be matter for further experiments.

To summarize, dielectric measurements of the rigid and planar 1-methylindole are performed at elevated pressures to solve the problem of finding at ambient pressure a single secondary relaxation but with properties at variance with the supposedly universal JG β -relaxation. The molecular anisotropy is a key ingredient only to separate different rotational motions in rigid systems. Two secondary relaxations are resolved at elevated pressures and temperatures from the fact that the slow β -relaxation is pressure sensitive but the fast β' -relaxation is not. From the pressure and temperature dependences of the slow β -relaxation time τ_β and the α -relaxation time τ_α , the invariance of the ratio τ_α/τ_β to changes of P and T at constant τ_α is observed. The properties of the slower β -relaxation prove that it is the JG β -relaxation, while the fast β' -relaxation originates from in-plane rotation. The coexistence of the JG β -relaxation with the β' -relaxation in 1MID is a novel finding in the dynamics of rigid van der Waals glass-formers.

ASSOCIATED CONTENT

Supporting Information

Additional data about (i) materials and methods, (ii) resolution of the slower secondary relaxation at sufficiently high pressures in isothermal data at 221 K, (iii) pressure dependence of T_g , (iv) demonstration of the enhanced resolution of the β -relaxation with pressure.

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Notes

The authors declare no competing financial interests.

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REFERENCES

- ¹ Ngai, K. L.; Paluch, M. Classification of secondary relaxation in glass-formers based on dynamic properties. *J. Chem. Phys.* **2004**, 120, 857-873.

- ² Capaccioli, S.; Paluch, M.; Prevosto, D.; Wang, L. M.; Ngai, K. L. Many-body nature of relaxation processes in glass-forming systems. *J. Phys. Chem. Lett.* **2012**, 3, 735-743.
- ³ Romanini, M.; Barrio, M.; Macovez, R.; Ruiz-Martin, M. D.; Capaccioli S.; Tamarit, J. Ll. Thermodynamic scaling of the dynamics of a strongly hydrogen-bonded glass-former, *Sci. Rep.* **2017**, 7, 1346.
- ⁴ Ngai, K. L.; Habasaki, J.; Prevosto, D.; Capaccioli. S.; Paluch M. Thermodynamic scaling of α -relaxation time and viscosity stems from the Johari-Goldstein β -relaxation or the primitive relaxation of the coupling model, *J. Chem. Phys.* **2012**, 137, 034511.
- ⁵ Ngai, K. L., Wang, L. M.; Yu, H. B. Relating ultrastable glass formation to enhanced surface diffusion via the Johari-Goldstein β -relaxation in molecular glasses, *J. Phys. Chem. Lett.* **2017**, 8, 2739-2744.
- ⁶ Johari, G. P.; Goldstein, M. Viscous liquids and the glass transition. II. secondary relaxations in glasses of rigid molecules. *J. Chem. Phys.* **1970**, 53, 2372-2388.
- ⁷ Ichitsubo, T.; Matsubara, E.; Yamamoto, T.; Chen, H. S.; Nishiyama, N.; Saida, J.; Anazawa, K. Microstructure of fragile metallic glasses inferred from ultrasound-accelerated crystallization in Pd-based metallic glasses. *Phys. Rev. Lett.* **2005**, 95, 245501.
- ⁸ Yu, H. B.; Wang, W. H.; Bai, H. Y.; Wu, Y.; Chen, M. W. Relating activation of shear transformation zones to β relaxations in metallic glasses. *Phys. Rev. B* **2010**, 81, 220201(R).
- ⁹ Wang, Z.; Sun, B. A.; Bai, H. Y.; Wang, W. H. Evolution of hidden localized flow during glass-to-liquid transition in metallic glass. *Nat. Commun.* **2014**, 5, 5823.
- ¹⁰ Wang, Q.; Zhang, S. T.; Yang, Y.; Dong, Y. D.; Liu, C. T.; Lu, J. Unusual fast secondary relaxation in metallic glass. *Nat. Commun.* **2015**, 6, 7876.
- ¹¹ Ngai, K. L.; Casalini, R.; Capaccioli, S.; Paluch, M.; Roland, C. M. Do theories of the glass transition, in which the structural relaxation time does not define the dispersion of the structural relaxation, need revision? *J. Chem. Phys. B* **2005**, 109, 17356-17360.

- ¹² Mierzwa, M.; Pawlus, S.; Paluch, M.; Kaminska, E.; Ngai, K. L. Correlation between primary and secondary Johari–Goldstein relaxations in supercooled liquids: Invariance to changes in thermodynamic conditions. *J. Chem. Phys.* **2008**, 128, 044512.
- ¹³ Kessairi, K.; Capaccioli, S.; Prevosto, D.; Lucchesi, M.; Sharifi, S.; Rolla, P. A. Interdependence of primary and Johari-Goldstein secondary relaxations in glass-forming systems. *J. Phys. Chem. B* **2008**, 112, 4470-4473.
- ¹⁴ Ngai, K. L. *Relaxation and Diffusion in Complex Systems*; Springer: New York, 2011.
- ¹⁵ Thayyil, M. S.; Ngai, K. L.; Prevosto, D.; Capaccioli, S. Revealing the rich dynamics of glass-forming systems by modification of composition and change of thermodynamic conditions. *J. Non-Cryst. Solids* **2015**, 407, 98-105.
- ¹⁶ Wagner, H.; Richert, R. Equilibrium and non-equilibrium type β -relaxations: D-Sorbitol versus *o*-Terphenyl. *J. Phys. Chem. B* **1999**, 103, 4071-4077.
- ¹⁷ Kudlik, A.; Benkhof, S.; Blochowicz, T.; Tschirwitz, C.; Rössler, E. The dielectric response of simple organic glass formers. *J. Mol. Struct.* **1999**, 479, 201-218.
- ¹⁸ Brand, R.; Lunkenheimer, P.; Loidl, A. Relaxation dynamics in plastic crystals. *J. Chem. Phys.* **2002**, 116, 10386-10401.
- ¹⁹ Romanini, M.; Negrier, Ph.; Tamarit, J. Ll.; Capaccioli, S.; Barrio, M.; Pardo, L. C.; Mondieig, D. Emergence of glassy-like dynamics in an orientationally ordered phase. *Phys. Rev. B* **2012**, 85, 134201.
- ²⁰ Hassine, B. B.; Negrier, Ph.; Romanini, M.; Barrio, M.; Macovez, R.; Kallel, A.; Mondieig, D.; Tamarit, J. Ll. Structure and reorientational dynamics of 1-F-adamantane. *Phys. Chem. Chem. Phys.* **2016**, 18, 10924-10930.
- ²¹ Singh, A. K.; Murthy, S. S. N. Johari-Goldstein relaxation in orientationally disordered phase of hexa-substituted benzenes. *Thermochim. Acta* **2015**, 604, 33-44.

- ²² Fragiadakis, D.; Roland, C. M. Dynamic correlations and heterogeneity in the primary and secondary relaxations of a model molecular liquid. *Phys. Rev. E* **2014**, 89, 052304.
- ²³ Qiao, J. C.; Pelletier, J. -M.; Casalini, R. Relaxation of bulk metallic glasses studied by mechanical spectroscopy. *J. Phys. Chem. B* **2013**, 117, 13658-13666.
- ²⁴ Zhu, Z. G.; Li, Y. Z.; Wang, Z.; Gao, X. Q.; Wen, P.; Bai, H. Y.; Ngai, K. L.; Wang, W. H. Compositional origin of unusual β -relaxation properties in La-Ni-Al metallic glasses. *J. Chem. Phys.* **2014**, 141, 084506.
- ²⁵ Jarosz, G.; Mierzwa, M.; Ziolo, J.; Paluch, M.; Shirota, H.; Ngai, K. L. Glass transition dynamics of room-temperature ionic liquid 1-methyl-3-trimethylsilylmethylimidazolium tetrafluoroborate. *J. Phys. Chem. B* **2011**, 115, 12709-12716.
- ²⁶ Böhmer, R.; Diezemann, G.; Geil, B.; Hinze, G.; Nowaczyk, A.; Winterlich, M. Correlation of primary and secondary relaxations in a supercooled liquid. *Phys. Rev. Lett.* **2006**, 97, 135701.
- ²⁷ Nowaczyk, A.; Geil, B.; Hinze, G.; Böhmer, R. Correlation of primary relaxations and high-frequency modes in supercooled liquids. II. Evidence from spin-lattice relaxation weighted stimulated-echo spectroscopy. *Phys. Rev. E* **2006**, 74, 041505.
- ²⁸ Bedrov, D.; Smith, G. D. Secondary Johari-Goldstein relaxation in linear polymer melts represented by a simple bead-necklace model. *J. Non-Cryst. Solids* **2011**, 357, 258-263.
- ²⁹ Li, X. Q.; Wang, M.; Liu, R. P.; Ngai, K. L.; Tian, Y. J.; Wang, L. -M.; Capaccioli, S. Secondary relaxation dynamics in rigid glass-forming molecular liquids with related structures. *J. Chem. Phys.* **2015**, 143, 104505.
- ³⁰ Liu, G.; Mackowiak, M.; Li, Y.; Jonas, J. Rotational diffusion of liquid toluene in confined geometry. *J. Chem. Phys.* **1991**, 94, 239-242.
- ³¹ Hinze, G.; Sillescu, H.; Fujara, F. Anisotropic motion of toluene above and below the glass transition studied by ^2H NMR. *Chem. Phys. Lett.* **1995**, 232, 154-158.

- ³² Hensel-Bielówka, S.; Paluch, M.; Ngai, K. L. Emergence of the genuine Johari-Goldstein secondary relaxation in *m*-fluoroaniline after suppression of hydrogen-bond-induced clusters by elevating temperature and pressure. *J. Chem. Phys.* **2005**, 123, 014502.
- ³³ Wang, M.; Li, X. Q.; Guo, Y. X.; Wu, T.; Liu, Y. D.; Ngai, K. L.; Wang, L. -M. A new secondary relaxation in the rigid and planar 1-methylindole: evidence from binary mixture studies. *J. Chem. Phys.* **2016**, 145, 214501.
- ³⁴ Outhouse, E. A.; Demmer, D. R.; Leach, G. W.; Wallace, S. C. Vibrational predissociation in S₁ 1-methylindole van der Waals clusters. *J. Chem. Phys.* **1993**, 99, 80-90.
- ³⁵ Srivastava, K. P.; Singh, V. K. Quantum chemical studies on conformations of indoles. *Der. Pharma. Chemica.* **2010**, 2, 385-393.
- ³⁶ Xiao, W.; Tofteskov, J.; Christensen, T. V.; Dyre, J. C.; Niss, K.; Isomorph theory prediction for the dielectric loss variation along an isochrone. *J. Non-Cryst. Solids* **2015**, 407, 190-195.
- ³⁷ Havriliak, S.; Negami, S. A complex plane representation of dielectric and mechanical relaxation processes in some polymers. *Polymer* **1967**, 8, 161-210.
- ³⁸ Sepúlveda, A.; Tyliniski, M.; Guiseppi-Elie, A.; Richert, R.; Ediger, M. D. Role of fragility in the formation of highly stable organic glasses. *Phys. Rev. Lett.* **2014**, 113, 045901.
- ³⁹ Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in glassforming liquids and amorphous solids. *J. Appl. Phys.* **2000**, 88, 3113-3157.
- ⁴⁰ Dyre, J. C. Colloquium: the glass transition and elastic models of glass-forming liquids. *Rev. Mod. Phys.* **2006**, 78, 953-972.
- ⁴¹ Adrjanowicz, K.; Kaminski, K.; Wojnarowska, Z.; Dulski, M.; Hawelek, L.; Pawlus, S.; Paluch, M.; Sawicki, W.; Dielectric relaxation and crystallization kinetics of ibuprofen at ambient and elevated pressure, *J. Phys. Chem. B* **2010**, 114, 6579–6593.
- ⁴² Hinze, G.; Sillescu, H. ²H nuclear magnetic resonance study of supercooled toluene: Slow and fast processes above and below the glass transition. *J. Chem. Phys.* **1996**, 104, 314-319.

- ⁴³ Rivera-Calzada, A.; Kaminski, K.; Leon, C.; Paluch, M. Ion dynamics under pressure in an ionic liquid. *J. Phys. Chem. B* **2008**, 112, 3110-3114.
- ⁴⁴ Chen, Z.; Nozaki, R. Does transparent nematic phase exist in 5CB/DDAB/water microemulsions? From the viewpoint of temperature dependent dielectric spectroscopy. *J. Chem. Phys.* **2011**, 134, 034505.
- ⁴⁵ Brás, A. R.; Dionísio, M.; Huth, H.; Schick, Ch.; Schönhals, A. Origin of glassy dynamics in a liquid crystal studied by broadband dielectric and specific heat spectroscopy, *Phys. Rev. E* **2007**, 75, 061708.
- ⁴⁶ Elmahdy, M. M.; Floudas, G.; Mondeshki, M.; Spiess, H. W.; Dou, X.; Mullen, K. Origin of the complex molecular dynamics in functionalized discotic liquid crystals. *Phys. Rev. Lett.* **2008**, 100, 107801.
- ⁴⁷ Haase, N.; Grigoriadis, C.; Butt, H.; Müllen, K.; Floudas, G. Effect of dipole functionalization on the thermodynamics and dynamics of discotic liquid Crystals. *J. Phys. Chem. B* 2011, 115, 5807-5814.